Regeneration of Oils Used for Deep Frying: A Comparison of Active Filter Aids

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A number of products are promoted for the purpose of regenerating used frying oils. These materials are referred to as "active" filter aids. They are purported to adsorb polar compounds, which are the products of oil degradation, and to retain them for removal by filtration. To evaluate some of these materials, portions of a used oil were treated with each of several "active" filter aids and filtered in a commercial-type recirculating oil filter. The triglycerides and any adsorbed compounds were extracted from the filter cake with a series of increasingly polar organic solvents. The composition of each of the filter cakes was quantitatively determined. The materials tested in this study were diatomaceous earth, acid-activated bleaching earth, activated aluminas, silica, carbon and synthetic magnesium silicate. Significant differences in the adsorbent characteristics of the materials were found. Adsorption of polar oil degradation compounds ranged from 2 mg of polar compounds per gram of diatomaceous earth to about 200 mg/g magnesium silicate.

KEY WORDS: Active filter aid, adsorbent, frying, oil degradation.

Deep-fat frying is a popular way to prepare a variety of foods. When food is fried in heated oil, many complex chemical reactions occur and the oil begins to degrade (1). The triglyceride molecule breaks down into both volatile and nonvolatile compounds which are soluble in the oil. These components contribute to both the desirable and undesirable sensory characteristics of the food fried in the oil.

Natural triglycerides comprising an oil are considered nonpolar material. The products of oil degradation are defined as polar compounds by the International Union of Pure and Applied Chemistry Method 2.507 (2). The polar components of a degraded oil are free fatty acids, mono- and diglycerides, oxidized triglycerides and oligomeric triglycerides (polymers). Several European countries have placed legal limits on the amount of total polar material that may be present in an oil used for deep-fat frying (3). A positive correlation between the quality of food fried in oil and the concentration of total polar materials present in the frying oil has been reported (4).

During the frying process, the concentration of degradation products gradually increases, and the oil quality deteriorates until the oil is unfit for further use. The quality of food fried in the oil correspondingly decreases until it is unacceptable. It is common practice for restaurant owners and managers to filter oil used for deep-fat frying to remove food debris, which may accelerate the decomposition of the oil. The removal of particulate material alone is known as passive filtration. Simultaneous removal of particles by filtration and soluble impurities by adsorption (active filtration) is more desirable because it will provide higher-quality fried foods and will extend the life of the oil.

Several materials, either alone or as a component of a blend, are purported to adsorb the polar degradation products present in a heated oil. Among these are synthetic magnesium silicate (5), alumina (aluminum oxide), acid activated bleaching earth (6), activated carbon (7–10) and various forms of silica (10–14).

Previously, a comparison of these materials was made by saturation of the adsorption sites with polar frying oil degradation products (15). A degraded frying oil was dissolved in a nonpolar solvent and passed through a column of the adsorbent until the concentration of polar materials in the effluent was the same as the concentration in the influent solvent solution. A major concern for evaluation of adsorbents by this method is that the adsorption kinetics would be different for adsorption of polar degradation compounds from a solution of the used oil in a nonpolar solvent than for adsorption directly from the used triglyceride. To address this in the present study, portions of a used frying oil were batch-treated with each of the adsorbents. The adsorbed polar compounds were removed from the filter cake by solvent extraction and quantitatively determined by high-performance size-exclusion chromatography (HPSEC).

MATERIALS AND METHODS

The specific products chosen to represent the materials evaluated are listed in Table 1. This table also lists some of the common physical and chemical properties of the materials tested. Diatomaceous earth was included in the test as a control, because it was not expected to adsorb any polar compounds (15). The pH was determined on a 5% by weight suspension of filter aid in deionized water. The percent weight loss on drying (% LOD) was determined by drying the materials in an oven at 105°C for 2 h (16). The additional percent weight loss on ignition (% LOI) was determined by ignition of the dry sample at 900°C for 1.5 h (16). This value is calculated as a percent of the dry weight remaining after the LOD test. Surface area was determined by nitrogen adsorption (17) with a Model 2200 high-speed surface area analyzer (Micromeritics Instrument Corp., Norcross, GA). The values in Table 1 are the results of at least two analyses of each material.

A large quantity of used vegetable oil (partially hydrogenated soybean oil), which had been used to fry french fries, was obtained from a local fast food restaurant. The oil had degraded to the restaurant's normal discard point. The oil was filtered through the restaurant's standard filter paper to remove particulate material, placed in a large stainless steel pot with a stainless steel spigot at the bottom and heated to 150°C ± 4°C with continuous stirring.

We built a one-quarter scale commercial-type recirculating oil filter to have a maximum capacity of 2 gal of oil and a filter area of 84 in^2. Preparing the filter with the same type of filter paper the restaurant uses, 1.3 gal

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TABLE 1

Common Physical and Chemical Properties of the Materials Tested

Material	Trade name	pH	%LOD[a]	%LOI[b]	Surface area m^2/g
Activated carbon	Darco T-88[c]	8.00	4.8	90.6	824
Acidic pH alumina	Brockmann I[d]	4.30	<1.0	2.8	167
Neutral pH alumina	ABA 6000[e]	6.55	11.5	18.1	312
Basic pH alumina	A-2[f]	9.55	0.1	7.7	787
Bleaching earth	Filtrol 105[g]	3.80	15.2	5.6	311
Diatomaceous earth	FW-18[h]	9.60	0.1	0.2	<10
Magnesium silicate	Magnesol XL[i]	8.50	10.8	10.9	619
Silica	TriSyl[j]	2.75	65.6	3.9	955

[a] LOD—loss on drying at 105°C for 2 h. [b] LOI—additional loss on ignition at 900°C for 1.5 h (% of dry basis weight). [c] American Norit Co., Jacksonville, FL. [d] Aldrich Chemical Co., Milwaukee, WI. [e] Selecto Inc., Kennesaw, GA. [f] LaRoche Chemicals, Baton Rouge, LA. [g] Harshaw Filtrol, Cleveland, OH. [h] Eagle Picher, Reno, NV. [i] Dallas Group of America Inc., Liberty Corner, NJ. [j] WR Grace & Co., Baltimore, MD.

of hot oil was drained into the filter and 41.0 g of adsorbent (approximately 1% by weight of the oil) as received from the vendor was added with mixing. The oil was recirculated through the filter cake for 5 min and then pumped to a storage container. To assure that the cake was as dry as possible, vacuum was continued 1 min beyond the point when no more liquid flowed through the return hose. The filter cake was carefully removed from the filter, separated from the paper, weighed and stored in a sealed jar under nitrogen. The filter was thoroughly cleaned and the procedure was performed with the next adsorbent. Samples were taken of initial oil for each adsorbent test and analyzed by HPSEC to assure that the oil was not degrading.

HPSEC (also known as gel permeation chromatography) is a facile method to separate and quantify the high- and low-molecular weight components of a used frying oil (18,19). The HPSEC system consisted of a Micromeritics Model 725 autosampler, a Varian Model 5000 HPLC, a Varian RI-4 refractive index detector and a Varian Model 4270 integrator (Varian Associates, Sugar Land, TX). Tetrahydrofuran (THF) with approximately 200 mg/L butylated hydroxytoluene added as a stabilizer was used for the mobile phase at a rate of 1.0 mL/min.

The column system consisted of stainless-steel columns (3–25 cm by 7.8 mm) packed with polystyrene-divinyl benzene polymer (5 μm diameter). The system was a Phenogel guard column (Phenomenex, Torrence, CA), followed by two G2500HXL columns (500 Å) connected in series with a G2000HXL column (250 Å) (Supelco Inc., Bellefonte, PA). Column temperatures were held at 30°C. Figure 1 is a chromatogram of the analysis of the initial used frying oil with this system.

The composition of the initial used oil and extraction residues was determined by the external standard method. Detector response factors required for integration were determined by analysis of a pure soybean oil (Wesson), fatty acid standards (oleic and stearic acids) and mono- and diglyceride standards obtained from Sigma Chemical Co. (St. Louis, MO).

Three 10-to-20 g samples of each filter cake were separately placed in Soxhlet extractors and serially extracted with increasingly polar organic solvents to remove both adsorbed oil and polar compounds: Extraction #1 was petroleum ether, Extraction #2 was diethyl ether, Extraction #3 was methanol and Extraction #4 was methanol with sodium hydroxide.

The first extraction with petroleum ether was intended to remove the oil that coated the particles or was trapped in the pores and spaces between particles. It was expected that the oil removed in this extraction would have almost the same composition of triglycerides and polar compounds as the initial oil. The only expected difference would be in the polar compounds adsorbed by the filter aid.

Two successive extractions were with progressively polar solvents: diethyl ether followed by methanol. The final step was digestion with 0.1N NaOH in methanol. These solvents were intended to remove any polar compounds adsorbed by the active filter aids. The petroleum ether and diethyl ether extractions were carried out for 5 h. The methanol extractions were continued for 16 h. The diethyl ether and methanol extracts were collected separately, and the solvents were carefully removed by evaporation on a steam bath.

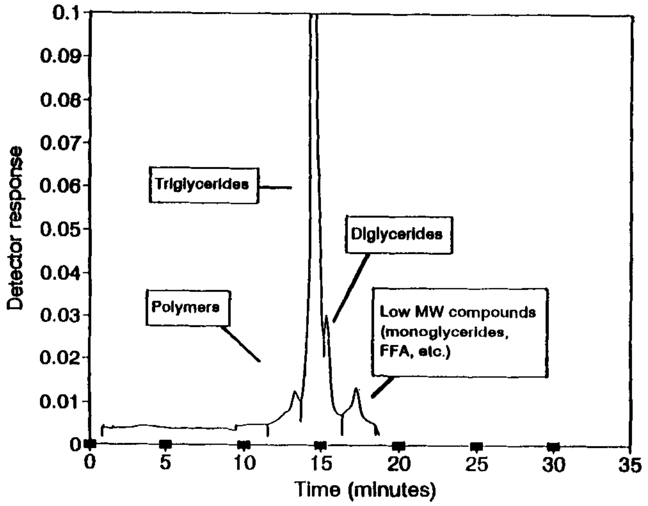

FIG. 1. High-performance size-exclusion chromatography chromatogram of initial used frying oil. Abbreviations: MW, molecular weight; FFA, free fatty acids.

The residual cake was mixed with the NaOH in methanol solution and stirred for 30 min at 50°C. The mixture was placed in a filtration funnel and washed with a mixture of methanol and water to remove the NaOH. The pH of the filtrate was adjusted to 4–5, then extracted with chloroform. The chloroform was removed in a roto-evaporator and the residue was handled the same as the other extraction residues.

The residues from each extraction were redissolved in THF and analyzed by HPSEC to determine their composition. The amount of THF used to dissolve the residues was adjusted so that 50 to 100 μg of material was injected into the chromatographic system. Each sample was analyzed in triplicate, and the values reported in Table 3 are the average of the three analyses.

As an error analysis, six samples of the magnesium silicate filter cake were extracted and analyzed by this method. The standard deviations of the extraction residue weights and HPSEC analyses of the extracted materials are included in Tables 2 and 3 below the values for the magnesium silicate. The magnesium silicate cake was chosen for this because it had adsorbed the most total polar materials.

RESULTS AND DISCUSSION

Table 2 lists the total weight of the filter cake, the weight percent composition as determined by the extractions from the three portions and the calculated weight of each component fraction.

With only a few exceptions, the HPSEC analysis showed that the oil extracted by the petroleum ether had approximately the same composition as the initial oil (Table 3). This indicates that this extraction removed only the oil that was trapped in the pores or absorbed on the surface of the materials.

The HPSEC data in Table 3 show that the residue removed from the adsorbents by the polar solvents consisted almost entirely of polar oil degradation products (polymers, diglycerides, monoglycerides, free fatty acids, *etc.*). There does not appear to be any pattern to the removal of polar compounds from the adsorbents by the increasingly polar solvents.

Using the initial weight of the adsorbent filter cake (column 1 of Table 2), the average percent composition of the three replicate cake portions (Table 2), and the percent composition of the extraction residues (Table 3), the weight of each component of the filter cake was calculated (Table 3). The combined weight of all of the polar components extracted is the weight of total polar compounds adsorbed (Table 4). The adsorptivity per gram of adsorbent (Table 4) was calculated by dividing the total weight of polar compounds extracted by the initial 41 g of adsorbent used (as received).

The diatomaceous earth adsorbed almost no polar compounds from the oil. Some of the adsorbents demonstrated selective adsorptivity (*i.e.*, they primarily adsorbed only one class of polar compounds). The best example of this is the aluminas, which primarily adsorbed free fatty acids, monoglycerides, *etc.* It is interesting that all of the aluminas adsorbed about the same amount of total polar compounds, regardless of their pH. The bleaching earth, magnesium silicate and silica adsorbed a great amount of polymer from the oil in addition to various amounts of the other polar compounds. The synthetic magnesium silicate adsorbed the highest amount of both polymers and low-molecular-weight materials from the used oil. It adsorbed approximately 200 milligrams of total polar compounds from the used frying oil per gram of adsorbent.

In the present study, the adsorptivity per gram was significantly higher for all of the adsorbents tested than in the previous study (15). The difference in these results and those previously reported is probably due to the adsorption kinetics of the two test procedures.

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TABLE 2

Total Weight of Filter Cake, Average Weight Percent Extracted by Each Solvent, Calculated Weight of Material Extracted from the Cake and the Calculated Weight of Solid Residue

		Average weight percent				Calculated weight extracted				
Adsorbent	Filter cake weight	Ext. #1	Ext. #2	Ext. #3	Ext. #4	Ext. #1	Ext. #2	Ext. #3	Ext. #4	Weight dry residue
Activated carbon	98.1	52.78	2.25	0.40	0.66	51.77	2.20	0.39	0.65	43.09
Alumina (acidic)	69.8	39.98	3.04	1.08	0.64	27.91	2.12	0.75	0.45	38.50
Alumina (neutral)	65.8	39.53	2.72	1.76	1.06	26.01	1.79	1.16	0.70	36.10
Alumina (basic)	64.9	39.79	2.79	2.28	0.96	25.82	1.81	1.48	0.62	35.17
Bleaching earth	56.5	41.18	3.59	5.20	0.54	23.27	2.03	2.94	0.31	28.00
Diatomaceous earth	112.8	63.65	0.04	0.04	0.03	71.80	0.45	0.45	0.34	39.76
Magnesium silicate	111.5	61.92	4.87	2.59	0.71	69.04	5.43	2.89	0.79	33.35
SD[a]		± 0.27	± 0.11	± 0.21	± 0.07					
Silica	64.5	65.08	9.06	1.47	0.10	41.98	5.84	0.95	0.06	15.67

[a] Standard deviation (SD) of six extractions (Ext.) from the magnesium silicate filter cake.

TABLE 3

Percent Composition by HPSEC of Initial Used Frying Oil and Residues Extracted from Filter Aids[a]

	Residue weight	Average percent composition (by HPSEC)				Calculated weight of extracted components (in grams)			
		POL	TG	DG	LMW	POL	TG	DG	LMW
Initial used frying oil (SD)[b]		4.9 ± 0.4	69.8 ± 1.8	16.4 ± 0.4	9.1 ± 0.9				
Extraction #1: petroleum ether (nonpolar solvent)									
Activated carbon	51.77	4.1	70.8	16.8	8.3	0.11	36.64	8.72	4.31
Alumina (acidic)	27.91	4.5	70.6	15.7	9.2	1.26	19.70	4.39	2.56
Alumina (neutral)	26.01	4.0	68.9	18.3	8.9	1.03	17.91	4.76	2.31
Alumina (basic)	25.82	4.7	70.1	18.1	7.1	1.20	18.11	4.66	1.84
Bleaching earth	23.27	4.9	67.5	17.8	9.7	1.15	15.72	4.15	2.27
Diatomaceous earth	71.80	5.1	69.9	15.6	9.4	3.64	50.21	11.22	6.73
Magnesium silicate	69.04	4.8	67.4	19.9	7.9	3.31	46.53	13.74	5.45
(SD)[c]		± 0.51	± 1.05	± 0.84	±1.04				
Silica	41.98	4.6	71.1	16.0	8.2	1.93	29.86	6.73	3.46
Extraction #2: diethyl ether									
Activated carbon	2.20	0.0	21.3	33.8	44.6	0.00	0.47	0.74	0.96
Alumina (acidic)	2.12	2.8	2.9	3.6	90.7	0.06	0.06	0.08	1.93
Alumina (neutral)	1.79	2.9	2.8	4.5	89.8	0.05	0.05	0.08	1.61
Alumina (basic)	1.81	4.1	9.3	14.6	72.0	0.07	0.17	0.27	1.30
Bleaching earth	2.03	28.9	14.1	16.0	41.0	0.59	0.29	0.32	0.83
Diatomaceous earth	0.45	63.6	15.1	10.3	11.0	0.03	0.01	0.01	0.01
Magnesium silicate	5.43	17.3	8.3	15.0	59.5	0.94	0.45	0.81	3.23
(SD)[c]		± 0.85	± 0.61	± 1.21	± 1.44				
Silica	5.84	14.7	27.5	32.2	25.6	0.86	1.61	1.88	1.49
Extraction #3: methanol									
Activated carbon	0.39	0.0	6.7	19.1	74.2	0.00	0.03	0.08	0.29
Alumina (acidic)	0.75	0.0	0.0	2.2	97.9	0.00	0.00	0.02	0.74
Alumina (neutral)	1.16	0.0	3.8	5.8	90.3	0.00	0.04	0.07	1.05
Alumina (basic)	1.48	2.9	6.4	11.4	79.3	0.04	0.09	0.17	1.17
Bleaching earth	2.94	27.6	13.7	16.7	42.4	0.81	0.40	0.49	1.25
Diatomaceous earth	0.05	29.2	20.1	12.1	38.8	0.01	0.01	0.00	0.02
Magnesium silicate	2.89	13.1	15.9	16.8	54.0	0.38	0.46	0.49	1.56
(SD)[c]		± 2.80	± 4.11	± 1.78	± 6.64				
Silica	0.95	38.0	11.3	15.8	34.9	0.36	0.11	0.15	0.33
Extraction #4: basic methanol									
Activated carbon	0.65	0.3	0.9	2.2	96.6	0.00	0.01	0.01	0.63
Alumina (acidic)	0.44	0.9	2.2	2.3	94.7	0.00	0.01	0.01	0.42
Alumina (neutral)	0.70	0.3	0.9	0.0	98.8	0.00	0.01	0.00	0.69
Alumina (basic)	0.62	5.8	3.9	1.7	88.6	0.04	0.02	0.01	0.55
Bleaching earth	0.31	8.9	11.0	17.9	62.2	0.03	0.03	0.05	0.19
Diatomaceous earth	0.03	10.4	12.1	11.3	69.6	0.00	0.00	0.00	0.02
Magnesium silicate	0.79	6.8	8.4	17.2	67.8	0.05	0.07	0.14	0.54
(SD)[c]		± 3.35	± 2.07	± 1.34	± 3.98				
Silica	0.06	4.9	6.9	10.7	77.1	0.00	0.00	0.01	0.05

[a] Abbreviations: POL—polymers, TG—triglycerides, DG—diglycerides, LMW—low molecular weight compounds (free fatty acids, monoglycerides, *etc.*).

[b] Standard deviation (SD) of high-performance size exclusion chromatography (HPSEC) analysis of initial used frying oil.

[c] SD of HPSEC analysis of residue extracted from magnesium silicate.

TABLE 4

Total Weight (in grams) of Compounds Extracted from the Filter Cakes by Polar Solvents

Adsorbent	POL	TG	DG	LMW	Total polar compounds	Adsorption[a] mg polars/g
Activated carbon	0.00	0.50	0.83	1.90	2.74	67
Alumina (acidic)	0.06	0.07	0.10	3.09	3.25	79
Alumina (neutral)	0.05	0.10	0.15	3.34	3.54	86
Alumina (basic pH)	0.15	0.29	0.44	3.03	3.63	89
Bleaching earth	1.43	0.72	0.87	2.27	4.47	109
Diatomaceous earth	0.04	0.02	0.01	0.05	0.10	2
Magnesium silicate	1.37	0.98	1.44	5.33	8.14	199
Silica	1.22	1.72	2.04	1.88	5.14	125

[a] The mg of total polar material adsorbed per gram of active filter aid. See Table 3 for abbreviations.

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